

Water Quality Review: Sierra Nevada 2006 Lake Monitoring

Neil Berg
Pacific Southwest Research Station, USDA Forest Service

April 2007



Executive Summary

Fifteen lakes in eight Class I and one Class II Wilderness Areas were sampled for acid-base water chemistry and water transparency between July and October 2006 as part of Project LAKES, the Sierra Nevada long-term lake monitoring project of the Pacific Southwest Region, USDA Forest Service Air Resources Program. In addition, twenty-nine lakes in John Muir (JM) and Hoover (HO) Class I Wildernesses were synoptically

sampled; several of these lakes are potentially good candidates for addition in 2007 to the long-term monitoring network.

An intent of the monitoring project is long-term monitoring of lakes in all ten Class I Areas in the Sierra Nevada, southern Cascades, and northeastern California overseen by the Pacific Southwest Region of the USDA Forest Service (one Class I Area in the southern Sierra Nevada, Domeland, has no lakes). To meet this objective appropriate lakes need to be identified in the relevant Class I Areas. This sub-objective will probably be reached this year when lakes from the last two remaining Wildernesses (JM and HO) will be selected for long-term monitoring and will be sampled for the second time.

Five long-term monitoring lakes have records of between 6 and 21 years in length, long enough for preliminary statistical analysis for temporal change. None of these lakes experienced a significant decline in the primary indicator for acidification, acid neutralizing capacity (ANC). A statistically significant decline in sulfate, however, was identified for Waca and Smith Lakes, both in Desolation Wilderness immediately west of Lake Tahoe. At Waca the sulfate change is slight, from the 4-6 $\mu\text{Eq L}^{-1}$ range between 1985 and 1992 to the 2-3 $\mu\text{Eq L}^{-1}$ range since 2000; with the lowest recorded value, 1.7 $\mu\text{Eq L}^{-1}$, in 2006. A similarly slight reduction in sulfate concentrations was identified at Smith Lake. Waca Lake also experienced a minor decrease in calcium concentration over time and a minor increase in ammonium. No other temporal changes were identified for any of the five lakes having 6 or more years of data. Because no other changes were identified, and the duration of records at most lakes is still short, these changes do not appear to warrant further assessment at this time.

A quality assurance review of the chemistry data identified a continuing “rebound” in the quality of the chemical analyses from 2004. For several metrics, the 2006 results are generally on a par with the pre-2004 results. For instance, appreciably more of the samples were analyzed at a “higher quality” level for percent ion differences in 2006 than in 2004 or 2005.

Ion imbalances evident in prior years persisted in 2006. This continuing imbalance suggests that one or more constituents causing the imbalance are not currently being analyzed.

Lakes in most of the Wildernesses sampled are sensitive to potential acidification, with ANC less than 50 $\mu\text{Eq L}^{-1}$ for many lakes in most Wildernesses. From synoptic data collected since 2000, concentrations for most chemicals are similar among seven of the Wildernesses (Dinkey, Kaiser, Emigrant, Mokelumne, Desolation, Thousand Lakes and Caribou). Higher, and more variable, concentrations are evident in Wildernesses with lakes in the eastern part of California (Ansel Adams, John Muir, Hoover and South Warner). Baseline data for major cation and anion concentrations are provided as well as levels of conductivity, ANC and pH.

In 2004 two lakes, Dana and Kidney, in northern Ansel Adams Wilderness had high sulfate concentrations. Several lakes sampled this year in HO had even higher sulfate

concentrations. The locations of these lakes are immediately east of several high-sulfate lakes in Yosemite National Park. Although the cause of the high sulfate isn't conclusively known, it is thought to be of geologic origin.

Recommendations

1) Continue sampling at the “long-term” monitoring lakes.

The lake sampling is aimed at identifying human-caused changes in lakes in the Sierra Nevada. Because changes can be subtle several years are needed before supportable interpretations about trends in lake chemistry can be made. In 2007 the network of long-term monitoring lakes will be complete and project costs should drop because fewer lakes will be sampled than in prior years. Continued sampling is needed to determine if the chemistry of the Wilderness lakes is changing, and if so if atmospheric deposition is a cause of the changes.

2) Select long-term monitoring lakes for HO and JM. The number of long-term monitoring lakes needs to be decided as well as the specific lakes.

JM has more lakes than any other Sierra Nevada Wilderness and JM is larger than any other Sierra Class I Area. These attributes suggest that JM should have a fair number of long-term monitoring lakes. Earlier analysis (Berg 2002) recommended seven long-term lakes for JM. This number still seems reasonable from a technical standpoint. Compared to the other ten Areas, HO is intermediate in both area and in number of lakes (19,669 hectares and 42 lakes). On this basis HO probably warrants one or two long-term monitoring lakes.

Because of the broad north-south extent of JM, and evidence of east-west chemical differences from the synoptic sampling, selection of geographically-spaced lakes in JM for long-term monitoring may be advisable. Several lakes with the lowest (or very low) sampled ANC (i.e. below $20 \mu\text{Eq L}^{-1}$) in JM (Bullet, Ram, East and West Twin Buck Lakes) are clustered together in the west central portion of the Wilderness. Potentially one of these could be selected for long-term monitoring. Stanford Lake, with $\text{ANC} = 18.8 \mu\text{Eq L}^{-1}$, is located at the far northeast and is also a candidate for long-term monitoring. Only one lake on the eastern or southern portion of JM has an ANC less than $40 \mu\text{Eq L}^{-1}$. This lake, Thunder and Lightning, plus Marshall Lake on the northwest, and Bench Lake on the southeast ($\text{ANC} = 31$ and $51 \mu\text{Eq L}^{-1}$ respectively), are potential long-term monitoring lakes. No lakes synoptically sampled in southern JM in 2006 had $\text{ANC} < 88 \mu\text{Eq L}^{-1}$, suggesting that Bench Lake may still be the best candidate for long-term monitoring in the southeastern section of JM. Alternatively, the ANC of Cottonwood 5B, at the extreme southern end of JM is $89 \mu\text{Eq L}^{-1}$. Cottonwood 5B is located directly east of wet and dry deposition monitoring locations in Sequoia National Park. These recommendations are based solely on lake location and measured ANC; other factors, like accessibility and location of air pathways should be incorporated into the decision-making process for JM long-term lakes.

3) Assess whether a dam on Smith Lake, a long-term monitoring lake, is dammed.

There is some evidence that Smith Lake, in Desolation Wilderness, is dammed. If it is, particularly with a cement barrier, the water chemistry of the lake may be unduly influenced by the dam, and use of Smith Lake for long-term monitoring should be reconsidered. In 2007 Smith Lake a field assessment is needed to determine the presence of a dam, and if one exists, its size and construction material.

4) Collect samples in early summer (as currently done) and early autumn at readily-accessible lakes to help determine if the sampling regime could be simplified to an early autumn collection solely at lake outlets.

In many lake sampling projects outlet samples are collected in autumn when the lake is thermally mixed and an outlet sample adequately represents the chemistry of the entire lake. Outlet sampling would be faster and potentially less costly than mid-lake sampling. Although research conducted in the 1980s in the Sierra suggest that lake chemistry may differ appreciably between early summer and early autumn, insufficient Forest Service data are currently available to determine if the chemistry of autumn outlet samples matches the chemistry of early-summer mid-lake samples. A decision to move to solely outlet sampling could be based on data from elsewhere, or from the 1980s Sierran research. Before making a decision on autumn outlet sampling a prudent approach is to concurrently collect both outlet and mid-lake samples at several long-term monitoring lakes at the end of snowmelt and again in early October, and compare the chemical concentrations. Several of these “seasonal” collections were conducted in 2006.

5) Assess the zooplankton data and decide whether to continue zooplankton sampling.

Zooplankton samples were collected for several years at the long-term monitoring lakes. Although zooplankton taxonomy and metrics were reported for most of these data, no comprehensive analysis or interpretation of these data has been done. A comprehensive interpretation of the available zooplankton data would provide input on whether continued collection of zooplankton samples is worthwhile.

6) Analyze a subset of the 2007 samples for dissolved organic carbon to attempt to explain the continuing ionic imbalance.

7) Clarify the status of Lower Cole Creek Lake.

Prior to 2006 Lower Cole Creek Lake had been sampled from 2002 through 2005 and was a long-term monitoring lake. In 2006 Lower Cole Creek Lake wasn't sampled. Documentation is needed to describe the status of Lower Cole Creek Lake; will it continue to be included in the monitoring network? If so why wasn't it sampled in 2006? If not why not?

In late March, 2007 decisions were made about some of the recommendations above. Specifically—

- Long-term lake monitoring will continue.
- Two lakes, Cascade and Moat, were provisionally selected for long-term monitoring in HO.

- Six lakes, Cottonwood 5B, East Wahoo, Vermillion, East Chain, Bench and Treasure, were provisionally selected for long-term monitoring in JM.
- Smith Lake was formally included into the long-term monitoring network. It has a small dam with a cement matrix, but Smith is a relatively large water body (particularly compared to the small size of the dam), its chemistry does not show excess calcium, and we believe the dam has probably long since leached out any calcium.
- Several lakes will be sampled at their outlets in late September.
- Lower Cole Creek Lake was sampled in 2006; it was mis-labeled initially.
- The Appendix of this document corrects the Lower Cole Ck Lake mis-labeling and includes a third 2006 set of samples collected at Powell Lk.

1.0 Introduction

Wilderness Areas are important national resources providing relatively unaltered natural landscapes for our enjoyment. Although watershed activities in Wildernesses are highly constrained, damage to some of these fragile resources is possible through long-range transport of air pollutants (Eilers 2003). For instance, Sickman et al. (2003) believe "...that lakes throughout the Sierra Nevada are experiencing measurable eutrophication in response to the atmospheric deposition of nutrients" and Fenn et al. (2003) document elevated nitrate levels in high-elevation Sierran lakes, reportedly from nitrogen deposition. To address this concern, in 2000 the Air Resources Program of the Pacific Southwest Region (Region 5) of the USDA Forest Service Forest Service initiated lake monitoring in Class I Wilderness Areas of the Sierra Nevada, California Cascades and northeastern California. A monitoring goal of this program is to provide early indication of possible impacts associated with deposition of acid-rain precursors.

This report assesses and interprets water chemistry data collected in 2006 and compares these data against information obtained in prior years. Lake transparency and zooplankton data are not addressed in the current report. This report does not directly specify the background context for lake or stream monitoring by the regional Air Resources Program. One objective of the monitoring, however, is to address the management goal of maintaining or improving aquatic, physical and biological air quality relate values (AQRVs) of "Class I" Wilderness Areas as mandated by amendments to the Clear Air Act and interpreted by the US Senate as an "affirmative responsibility by federal resource managers to err on the side of protecting AQRVs for future generations" (US Senate 1977).

2.0 Lake Monitoring Network

One intent of the Region 5 lake monitoring program is to follow the precedent of other FS regions by identifying a small number of lakes sensitive to atmospherically-driven acidification in each Class I Area and monitoring them over the long term. The premise is that monitoring lakes (operationally defined as water bodies greater than one hectare in area and greater than two meters in depth) particularly vulnerable to potential acidification will act as "a canary in a coal mine" and that their protection presupposes protection of less sensitive lakes.

Acid neutralizing capacity (ANC) is the single best indicator of lake sensitivity to acidification (Sullivan et al. 2001). Lakes with low ANC are sensitive to acidification, and low-ANC lakes provide information relevant to possible nutrient issues. The selection process for long-term monitoring lakes (those with low ANC) is not simple and requires a combination of modeling (Berg et al. 2005) and synoptic sampling prior to final selection. Fourteen long-term monitoring lakes were sampled in 2006. These lakes were selected after a one-time synoptic sampling of many lakes in each Wilderness in which ANC and other chemical constituents were evaluated. Future additions to the monitoring network will also be low-ANC lakes, and their selection will be partially based on information from synoptic sampling undertaken in 2006. By 2007 the

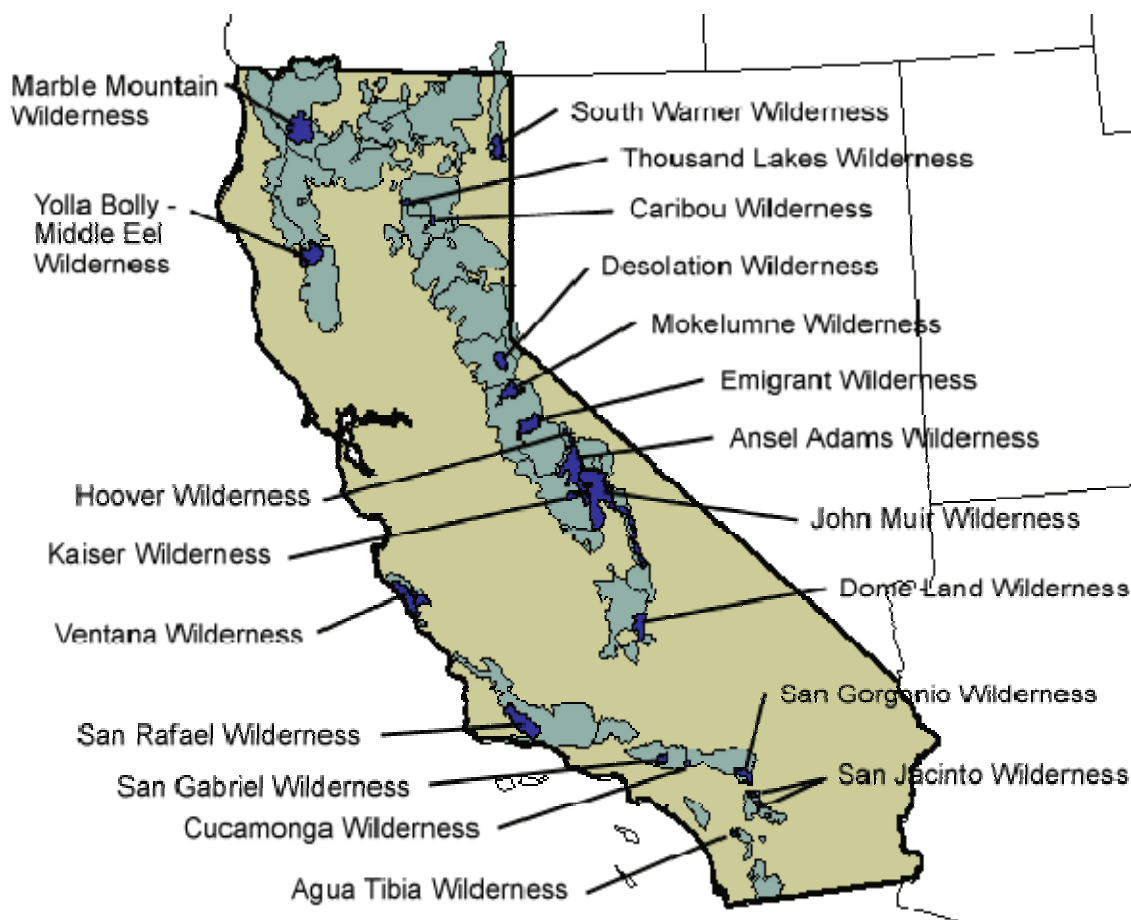
monitoring program will incorporate approximately 20 lakes in ten Class I Wildernesses ranging from the Sierra National Forest in the southern Sierra Nevada to the Modoc National Forest in the northeastern corner of California. In 2006 30 lakes were sampled from eleven Wildernesses as follows:

Wilderness	Number of Lakes Sampled	Long-term Monitoring Lakes
Hoover	10	0
John Muir	5	0
Kaiser	1	1
Ansel Adams	3	3
Dinkey Lakes	1	1
Mokelumne	2	2
Desolation	2	2
Emigrant	3	3
Caribou	1	1
1000 Lakes	1	1
South Warner	1	1

Two of the long-term monitoring lakes were sampled three times to begin to document any with-year temporal lake chemistry variation. Outlet as well as mid-lake samples were also collected at several of the long-term monitoring lakes, to provide information on the option to sample only outlets in the future.

One long-term monitoring lake, Waca in Desolation Wilderness, has been monitored eleven times since 1985; monitoring of the rest of the lakes began more recently:

Lake	Wilderness	Years of Data	Years Sampled
Powell	Emigrant	6	2000, 2002-06
Key	Emigrant	7	2000-06
Karls	Emigrant	4	2000, 2003-04, 2006
Long	Kaiser	6	2000, 2002-06
Patterson	S. Warner	5	2002-06
Mokelumne 14	Mokelumne	5	2002-06
Lower Cole Creek	Mokelumne	5	2002-06
Hufford	1000 Lakes	5	2002-06
Caribou 8	Caribou	5	2002-06
Waca	Desolation	11	1985, 1991-93, 2000-06
Smith	Desolation	7	1985-86, 1991-92, 2000, 2005-06
Walton	Ansel Adams	3	2004-06
Dana	Ansel Adams	3	2004-06
Little East Marie	Ansel Adams	3	2004-06
Bullfrog	Dinkey Lakes	3	2004-06



Besides the long-term monitoring lakes, since 2000 over 170 other lakes have been sampled in California Wildernesses administered by the USDA Forest Service. Fifteen lakes in JM and HO were synoptically-sampled in 2006 to identify candidate lakes for long-term monitoring. Their locations are mapped in Figures 1 and 2. Before summer 2007 several lakes in these Wildernesses will be selected for long-term monitoring, depending upon their sensitivity to acid precursors and other factors. With selection of long-term monitoring lakes in HO and JM, the Sierra Nevada lake monitoring network will be complete.

This report addresses lake chemistry in the context of an early-warning monitoring program for acidification of Wilderness lakes. The monitoring program is not a research study, and relatively minor irregularities in the quality assurance results are not presumed to be causes for major concern.

3.0 Objectives

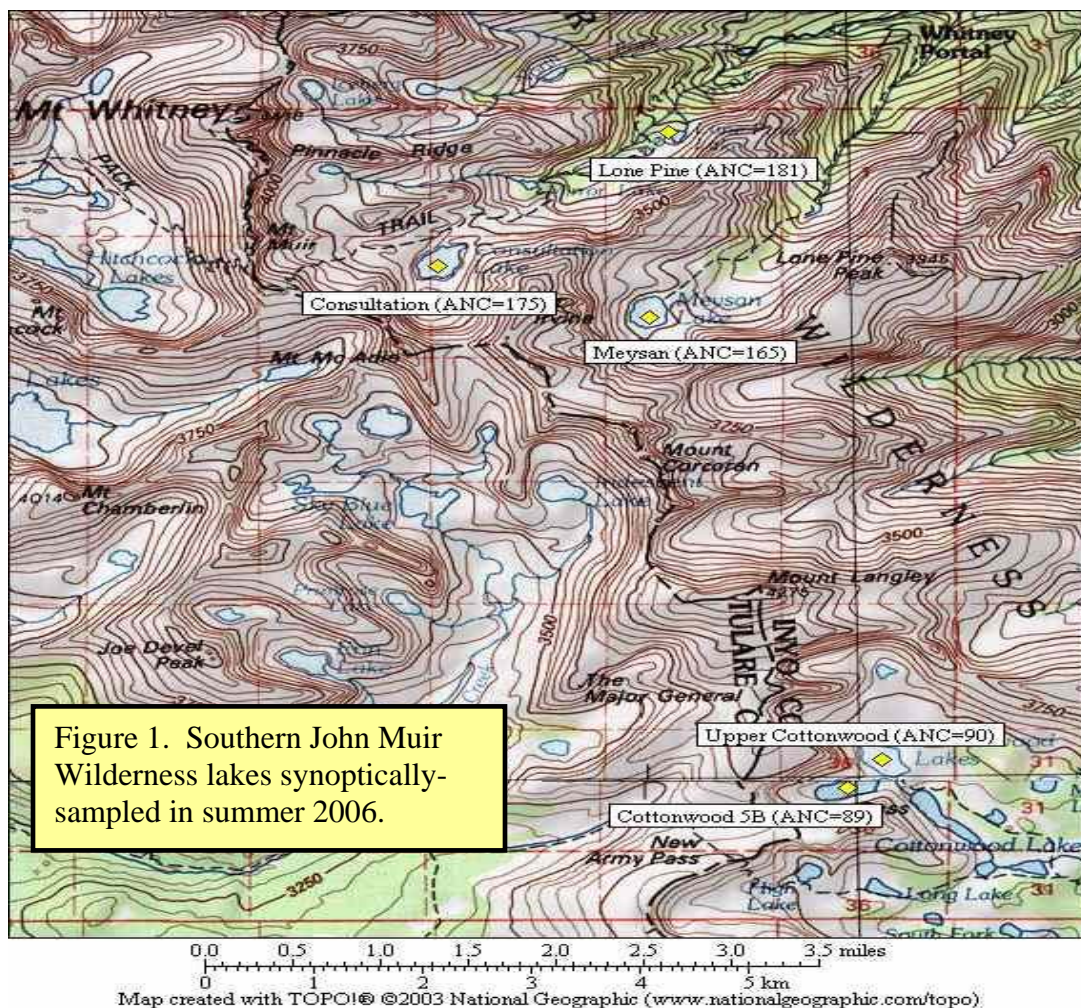
This report has six primary objectives:

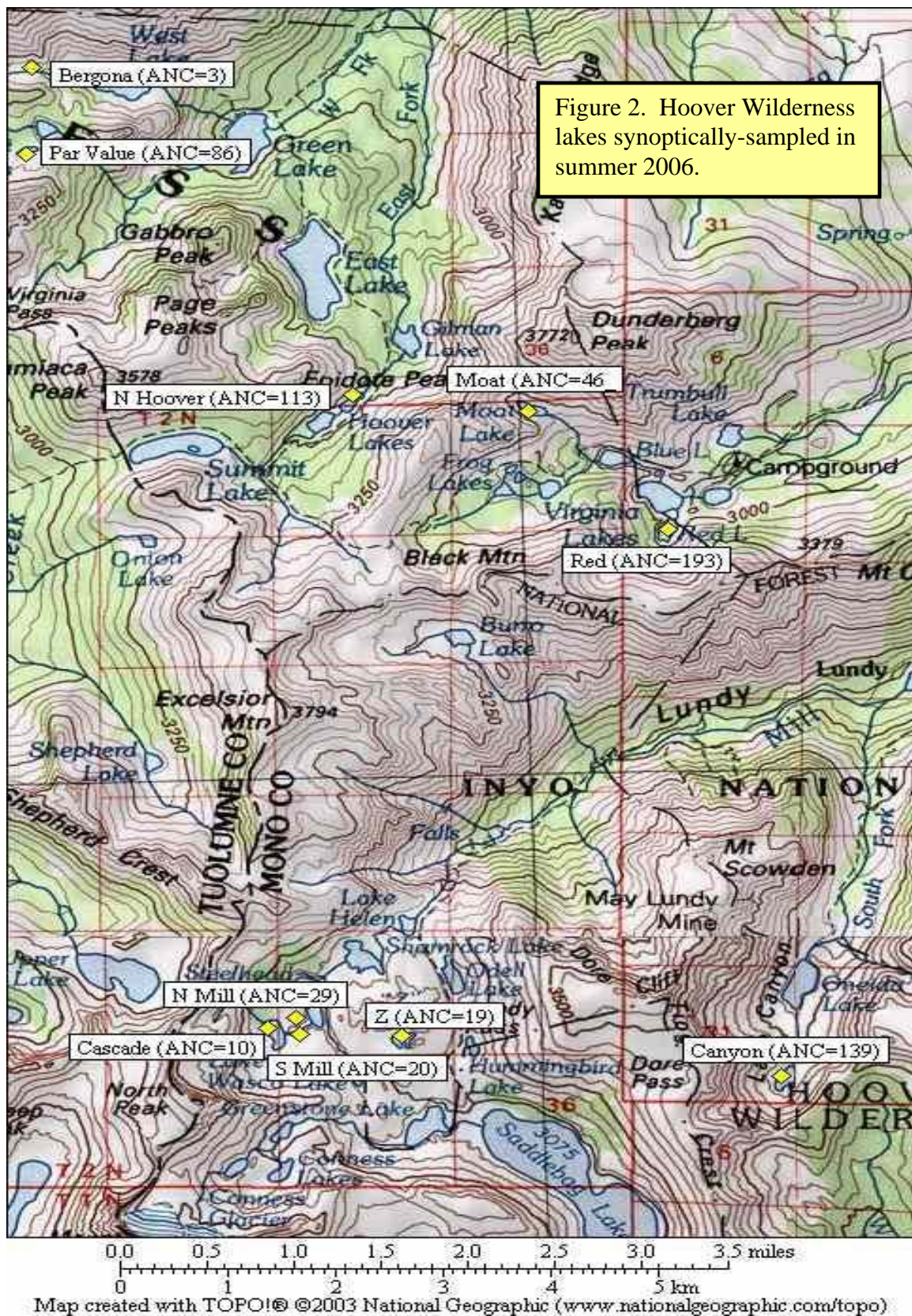
- 1) Assess the quality of selected field procedures and laboratory analyses of lake water samples collected in 2006, specifically to identify any samples that may need re-

analysis or that otherwise may require additional action (e.g., revision of sample type/label or deletion of the data).

- 2) Summarize the relationships between the 2006 lake chemistry and data collected in prior monitoring (e.g., trends through time).
- 3) Identify any differences in lake chemistries among the Class I Wildernesses (e.g., spatial variation).
- 4) Flag any lakes having unexpected chemical concentrations in JM and HO.
- 5) Identify candidate lakes for long-term monitoring in JM and HO.
- 6) Address the option of modifying the sampling regime to collect only outlet samples in early autumn, rather than mid-lake samples in early summer.

This report is not comprehensive in that some components of the 2006 (and earlier) data collection are not evaluated (e.g., data from field data sheets, including water temperature information, and zooplankton data). Nor are other potentially relevant components of the monitoring program comprehensively addressed (e.g., adequacy of training, dataset formalization).





4.0 Methods

To address the quality assurance objective, a variety of standardized techniques are available. This assessment focuses on commonly-used techniques described and exemplified in prior assessments for Forest Service lakes (e.g., Turk 2001, Eilers 2003, Eilers et al. 1998) and does not include all possible assessment procedures. The procedures evaluate (1) internal consistency of samples (e.g., transit time, ion balances, calculated versus measured ANC, calculated versus measured conductivity, and outlier assessment), (2) precision through analysis of duplicate samples, and (3) bias or contamination through assessment of field blanks. Each technique is described briefly below. The data were analyzed with either the Excel[®] or WQSTAT Plus[®] software packages.

All samples were analyzed at the USDA Forest Service Rocky Mountain Station analytical laboratory in Ft. Collins, Colorado (hereafter referred to as RM). Concentrations for the following constituents were assessed: conductivity, calcium, magnesium, sodium, potassium, ammonia, fluoride, chloride, nitrate, sulfate and acid neutralizing capacity. Acidity, as pH, was also evaluated.

Several of the long-term monitoring lakes were sampled both near the surface (epilimnion), and at depth (hypolimnion) if they were thermally stratified; otherwise the thermally un-stratified long-term lakes were sampled approximately 1 m below the lake surface. Samples from all of the JM and HO synoptically-surveyed lakes were collected at their outlets, or if an outlet wasn't found, along the shoreline. To begin to assess potential differences between mid-lake and lake outlet chemistries, several long-term monitoring lakes were sampled at all three locations contemporaneously (outlet, epilimnion and hypolimnion). Specific sampling and monitoring protocols are detailed in Berg and Grant (2004) for the long-term lakes and in Berg and Grant (2002) for the synoptically-sampled lakes.

Data analysis follows the draft protocol for long-term lake monitoring being adapted by the national Air Resources Program of the USDA Forest Service (Gurrieri 2006). The summarization objective addresses temporal change with time series plots and tests for statistical trends in chemistry for lakes with at least 6 years of data. The data are first checked for normality (Shapiro-Wilk procedure, Gilbert 1987), then trends are assessed by the nonparametric Mann-Kendall test, with statistically significant trends quantified by Sen's slope estimate (Sen 1968). Caution is needed in interpreting temporal trends because sampling over the years has been undertaken by different agencies and chemical analyses conducted at different laboratories. Differences in procedures could confound statistically significant temporal trends. Also the samples for trend analysis are from either mid-lake epilimnion or lake outflow locations. Although differences between these locations are typically understood to be minimal (Clow 2002, Musselman 2004), they could also confound identification of temporal trends.

Chemical differences among the Wildernesses are based on data collected from synoptic surveys in 2000, 2002, 2004, 2005 and 2006 and are assessed via the nonparametric

Mann-Whitney test among pairs of Wildernesses and by the Kruskal-Wallis test for comparison among three or more Wildernesses. Lakes with unexpected chemical concentrations are identified in the outlier assessment.

Recommendations for procedural changes, decisions needed and other actions are summarized at the beginning of this report and a listing of the 2006 chemistry data is given in Appendix I.

5.0 Results

Calculations for the results reported in this document were initially completed without knowledge of collection of epilimnion and outlet samples at Powell Lake in late October 2006 and with the impression that Mokelumne 14 Lake had been sampled twice. Actually Mokelumne 14 was sampled once and the “second” sample collection was at Lower Cole Creek Lake. The misunderstanding about Mokelumne 14/Lower Cole Creek has little bearing on most of the results. The absence of the October 2006 Powell Lake information does affect several aspects of the results reported here. Because the calculations are time-consuming and because it is thought that the absence of the October 2006 Powell Lake information does not materially influence most of the results, the October 2006 Powell Lake sample information is not included in the ion balance (section 5.1.1.2), calculated versus measured ANC (section 5.1.1.4), theoretical versus measured conductivity (section 5.1.1.5), outliers (section 5.1.1.6) and precision (section 5.1.2) determinations.

5.1 Quality Assurance

5.1.1 Internal Consistency

5.1.1.1 Transit Time

After collection, samples need to be kept cool to preserve their chemical integrity. Sample warming elevates the risk of biological activity in the sample that could alter the concentration of some chemical constituents. Although refrigerant is included in sample mailing packages the refrigerant has an unknown, but probably relatively short, effective lifespan. All effort should be made to assure sample arrival at the analytical laboratory as soon as possible after collection. To this end a courier system is sometimes used to expedite shipping of samples from lake to laboratory. If needed, samples are stored in a refrigerator rather than mailed over a weekend.

The critical time period is not the total transit time, but the duration that a sample is kept cool by a short-lived refrigerant (e.g., “blue ice”) versus a dedicated coolant (e.g., a refrigerator). Information is not readily available on the time duration samples were cooled by a short-lived refrigerant so the potential for sample degradation due to inadequate cooling can’t be completely assessed. Nevertheless, in general the longer the time between sample collection and receipt at the lab, the greater the chance for sample degradation.

Thirty-four sample collections were made from the 30 lakes sampled in 2006 (two lakes were sampled three times). Thirty-eight percent of the collections arrived at the laboratory within 3 days of sample collection (compared to 64% in 2003, 62% in 2004 and 26% in 2005). Almost 53% the collections in 2006 had transit times of 5 days or longer, with 11% of the samples in transit 11 or 12 day. 2005 also had a relatively high percentage of transits taking 5 or more days, but no prior year had any transits longer than 8 days. The 11 and 12 day transits were all from HO and no HO sample transit was quicker than 5 days. Reasons for the long transit times for the HO samples are not known. Chemical characteristics of the 11 and 12-day transit samples are addressed in a later section (5.1.3) of this report.

Although the long sample transit times for the HO samples is not a good sign, there will be no more synoptic sample collections so the transit times for the long-term lakes are more relevant to future project activities. The mean transit time for the 18 collections from the 14 long-term lakes was 4 days, a good transit duration given the distance of some of the lakes from overnight express mailing pickup locations.

Transit Time (days)	Number of Lakes				
	2006	2005	2004	2003	2002
1	1	1	0	0	1
2	6	8	14	3	6
3	6	2	4	4	3
4	3	7	0	2	25
5	6	4	4	1	5
6	2	15	5	0	1
7	6	4	1	1	1
8	0	1	1	0	0
>8	4	0	0	0	0

5.1.1.2 Ion Balance

A basic premise in ion balance determinations is that the sum of the negatively charged constituents (anions) should balance the sum of the positively charged constituents (cations) in each sample. Analytical procedures are not perfect so typically the ion balance is not exact for a set of samples. Ideally, however, there should be no bias; the sum of the cation minus anion concentrations for a set of samples should approximate zero. Bias is often attributed either to laboratory error or lack of testing for one or more cations or anions. Several related techniques address ion balance, either for potential problems with specific samples or as indicators of overall trends among samples.

Considered as a whole, the chemistry of the 2005 lake samples is biased (Figure 3), and has a consistent under-estimation of the anions or over-estimation of the cations. Over 97% of the 2006 non-blank samples have a greater cation sum than anion sum, and there is an overall average of 13.3 $\mu\text{Eq L}^{-1}$ cation excess/anion deficiency per sample. This

bias compares with averages in 2005, 2004, 2003, 2001 and 2000 of 16.4, 15.9, 9.1, 10.7 and 8.75 $\mu\text{Eq L}^{-1}$ respectively. A continuing cation excess/anion deficiency bias has been evident during every year of sample analysis, and by the average deficiency metric, the bias in 2006 reverses a worsening trend from the prior two years.

A four-quadrant plot (Figure 4) provides additional information on the cation excess-anion deficiency issue. This plot shows that the bias is best characterized as an under-estimation of anions, although some samples have an over-estimation of cations. Anion under-estimation has been consistent through all prior years of the project.

The ion balance problem has been evident during all years of sample collection. Samples from other dilute waters can have a similar imbalance, but the future utility of the data may be compromised until/unless a reason for the imbalance is determined. In past years both Jim Sickman and Joe Eilers independently suggested testing for dissolved organic carbon (DOC) to help determine if relevant constituents are not being analyzed. And both of these individuals also suggested that some samples (or split samples) be analyzed at a laboratory specializing in dilute waters. In 2004 a sub-set of samples was analyzed by a second laboratory. The second laboratory also identified cation underestimation. If funds are available, analysis for DOC should be undertaken in 2007 to help identify if lack of testing for DOC, or potentially some other constituent, is a cause of the ionic imbalance.

5.1.1.3. Cation and Anion Sums

The ion balance calculations in section 5.1.1.2 address the chemistry dataset as a whole. For individual samples Turk (2001) identified two triggering values for cation/anion sum problems—to meet “mandatory” and “higher-quality” levels of data quality:

Total Ion Strength (cations + anions) ($\mu\text{Eq L}^{-1}$)	% Ion Difference—Mandatory	% Ion Difference—Higher Quality
<50	>60	>25
50-100	>30	>15
≥ 100	>15	>10

Both sets of criteria are percent-based and take into account the fact that percentage values increase for the same absolute differences in concentrations as concentration levels decrease. The percent of samples meeting the two criteria are listed below for monitoring years 2002-2006:

Year	% Meeting Mandatory Criterion	% Meeting Higher Quality Criterion
2006	99	74
2005	91	73
2004	90	20
2003	100	83
2002	100	87

In comparison to earlier years, the 2006 data are of intermediate quality in that a higher percentage of the samples in 2006 than in 2004 and 2005 meet the higher quality criterion, but the 2006 percentages are lower than 2002 and 2003 for both the mandatory and higher quality criteria.

The one 2006 samples not meeting the mandatory criteria is from the outlet of Mokelumne 14, a long-term monitoring lake.

5.1.1.4 Calculated versus Measured ANC

Another index of potential ion imbalance is the comparison of measured ANC against ANC calculated as the difference in the sum of base cations (calcium + magnesium + sodium + potassium) and acid anions (sulfate + chloride + nitrate). A bias similar to the ion imbalance also exists for the 2006 ANC comparison (Figure 5). The calculated value on average is $11.6 \mu\text{Eq L}^{-1}$ greater than the measured value (compared to $15.8 \mu\text{Eq L}^{-1}$ greater in 2005, $15.65 \mu\text{Eq L}^{-1}$ greater in 2004 and $7.55 \mu\text{Eq L}^{-1}$ greater in 2003), with 94% of the individual samples having greater calculated than measured ANC. The $11.6 \mu\text{Eq L}^{-1}$ average is conditioned largely by five high-ANC samples from synoptically-monitored lakes, mostly in HO. Without these five samples the average calculated ANC drops to $9.1 \mu\text{Eq L}^{-1}$ greater than the measured value. Forty-three percent of the non-blank 2006 samples had calculated minus measured ANCs $> 10 \mu\text{Eq L}^{-1}$ (compared to 54% in 2005, 80% in 2004 and 27% in 2003). Eilers et al. (1998) label samples having calculated minus measured ANCs $> 5 \mu\text{Eq L}^{-1}$ as “outliers”. By this definition over 42% of the 2006 samples would be “outliers” (compared to 79% in 2005 and over 92% in 2004).

The imbalance between calculated and measured ANC is further evidence that either one or more constituents aren't being analyzed, or there are laboratory problems. By this measure the 2006 sample analysis is of higher quality than the 2005 and 2004 analyses.

The absolute value of the difference between measured and calculated ANC is greater than $30 \mu\text{Eq L}^{-1}$ for five samples collected from synoptic-sampled lakes in 2006: Canyon ($32 \mu\text{Eq L}^{-1}$ difference), North Hoover ($50 \mu\text{Eq L}^{-1}$), Lone Pine ($34 \mu\text{Eq L}^{-1}$), and both Red Lake duplicates (60 and $45 \mu\text{Eq L}^{-1}$).

5.1.1.5 Theoretical versus Measured Conductivity

The measured versus theoretical conductivities from the 2006 lake samples show most samples (86%) to be within the $\pm 1 \mu\text{S cm}^{-1}$ criteria used by Eilers et al. (1998) to identify “outlier” values (Figure 6). The 86% approximates earlier year percentages: 86 in 2005 and 88 in all three prior years. Several lakes with high calculated minus measured ANC also had high theoretical minus measured conductivity: Red duplicate, Lone Pine, and North Hoover.

Although there is some bias—70% of the non-blank samples have greater measured than calculated conductivity (compared to over 89% in 2005, 80% in 2004 and 75% in 2003)—the mean bias is small, $0.2 \mu\text{S cm}^{-1}$. Eilers (2003) described Gallatin National Forest lake samples with a slightly greater bias as not presenting “... a significant concern with respect to the quality of the data”.

Seven samples collected in 2006 exceeded Eilers et al.’s $\pm 1 \mu\text{S cm}^{-1}$ criteria. These samples were from Bullfrog epilimnion ($1.20 \mu\text{S cm}^{-1}$ difference), North Hoover ($-2.46 \mu\text{S cm}^{-1}$), Long epilimnion ($-1.30 \mu\text{S cm}^{-1}$), Consultation ($-1.00 \mu\text{S cm}^{-1}$), Lone Pine ($-1.07 \mu\text{S cm}^{-1}$), Bergona ($-1.02 \mu\text{S cm}^{-1}$), and Red duplicate ($1.89 \mu\text{S cm}^{-1}$).

5.1.1.6 Outliers

Outliers are extreme values that are inexplicable. Contamination by body contact with sample liquid, for instance, is typically identified by outlier values of sodium and chloride. For all 2006 non-blank samples, concentrations of calcium, sodium, magnesium, ANC, chloride, nitrate and sulfate are plotted in Figure 7. Outliers are assessed both visually and statistically using Dixon’s outlier test.

5.1.1.6.1 Visual assessment

Four samples, from three lakes in HO—Canyon, N Hoover and Red—had particularly high concentrations of calcium and sulfate, and high concentrations of ANC and magnesium compared to other samples collected in 2006. Because the duplicate samples from Red Lake have approximately equal concentrations for those constituents, the relatively high concentrations from this lake do not appear to be due to either a sample collection or laboratory error. Although the concentrations for the three lakes are high compared to most other samples collected in 2006, Dana Lake, 9 kilometers south of Canyon Lake, had high sulfate and nitrate concentrations when sampled in 2004, 2005 and moderately high sulfate in 2006. The high concentrations at Dana for three years running suggest that the concentrations there are real and not due to a procedural problem. Also, the close proximity of these lakes suggests that their high sulfate may be due to local influences, probably geologic in origin, and not a field sampling or lab analysis problem. High calcium and sulfate concentrations have generally not been found in other lakes synoptically sampled in project LAKES. Some lakes sampled in the 1985 Western Lake Survey (Landers et al. 1987) also had high calcium and sulfate concentrations (e.g., Hoover Lake in Hoover Wilderness with sulfate = $386 \mu\text{Eq L}^{-1}$ and calcium = $493 \mu\text{Eq L}^{-1}$). And lakes outside of the Sierra commonly have higher concentrations. For instance, the mean calcium and ANC concentrations of 1798 lakes surveyed in the Eastern Lake Survey were 245 and $264 \mu\text{Eq L}^{-1}$ respectively (Kanciruk et al. 1986).

Many ANC and calcium values plotted in Figure 7a are relatively high. Strong positive correlations between ANC and calcium (and often sodium and magnesium as well) are common (Landers et al. 1987) and pairing of high ANC with high calcium is not unexpected. Patterson Lake (in S Warner Wilderness) hypolimnion and epilimnion

samples (numbers 9 and 25 in Figure 7a), for instance, have relatively high ANC, calcium, sodium and magnesium concentrations. Similarly high concentrations of these constituents for this lake were recorded in prior years.

5.1.1.6.2 Statistical assessment

Dixon's outlier test (Dixon 1953, NIC 2005) assumes data are distributed normally or log normally and tests whether a suspect value fits the distribution of the rest of the data set. At the 0.05 level of statistical significance, Dixon's test identified one outlier, the lowest ANC value, $-5.9 \mu\text{Eq L}^{-1}$, for one of two duplicate samples from Bergona Lake in HO. No other outliers were identified for any other chemical constituent.

Although $-5.9 \mu\text{Eq L}^{-1}$ is a low ANC value, ANCs in the 0 to $10 \mu\text{Eq L}^{-1}$ range have been detected in other Sierran lakes, and Key Lk, a long-term monitoring lake in Emigrant Wilderness, recorded a negative ANC in 2001. Also, the ANC of the duplicate sample collected at Bergona was low, $2.9 \mu\text{Eq L}^{-1}$, implying that ANC was truly low at the time Bergona Lake was sampled. For these reasons, the low-ANC Bergona sample is not deleted from the dataset and is included in subsequent analyses.

5.1.2 Precision -- Duplicate Samples

Eighteen "duplicate" pairs of samples were collected in 2006 from shallow mid-lake locations (six samples from long-term monitoring lakes), at lake outlets (seven synoptically-collected lakes from JM and HO and five paired collections from long-term monitoring lakes), and one set of two samples from the hypolimnion of a long-term monitoring lake. All of these duplicates were collected not more than ten minutes apart. These duplicates should be nearly identical in their constituent concentrations. A measure of chemical variation, the percent relative standard deviation (%RSD), was calculated for all duplicates for ANC, calcium, nitrate, conductivity, magnesium, sodium, chloride, potassium and sulfate concentrations. Per B. Gauthier (5/30/02 email to J. Peterson) the %RSD for duplicate samples should be $\leq 10\%$. The following table lists the percentage of the pairs of duplicate samples with %RSD greater than 10% for samples collected between 2001 and 2006 for each constituent:

	2006	2005	2004	2003	2002	2001
<u>Number of Duplicate Pairs</u>	18	9	8	14	11	12
<u>Chemical Constituent</u>						
ANC	33	44	43	23	55	8
Calcium	0	11	14	38	36	25
Nitrate	61	0	29	8	0	9
Conductivity	0	22	0	46	18	17
Magnesium	0	11	29	8	36	8
Sodium	0	22	14	8	9	8
Potassium	22	22	57	8	18	8
Chloride	28	56	29	23	27	17

Sulfate	17	22	0	23	9	25
---------	----	----	---	----	---	----

For the %RSD metric, compared to earlier years and except for calcium, the 2006 duplicate samples were at least as precise as in most earlier years.

The %RSD calculation procedure is sensitive to “sample size”. Calculation of standard deviations on the basis of two values is marginal; typically at least three values are used, and ideally a much larger sample size should be the basis for the %RSD calculation. The relatively high values listed in the table above for some years may be partially due to this sample size effect.

Another reason for some relatively high %RSD values, particularly for nitrate, may be low concentrations, near or below the detection limit. For instance, the mean of the two nitrate duplicates from outlet samples taken from Powell Lake in 2006 was a very low $0.048 \mu\text{Eq L}^{-1}$. The individual concentrations were 0.032 and $0.065 \mu\text{Eq L}^{-1}$, also very low values. Nevertheless the %RSD for these duplicates is over 47%, much greater than the 10% threshold value. Also the 2006 median difference in nitrate duplicate concentrations is $0.05 \mu\text{Eq L}^{-1}$, a magnitude that is below the detection limit for nitrate. This low median difference in nitrate duplicate concentrations suggests that although the 2006 %RSD values for many nitrate duplicate are high, the absolute value of the differences is generally small. Last, prior to 2006 many samples had undetectable nitrate, and consequently relatively few %RSD values are available for those years.

ANC is the single best constituent for %RSD assessment because it tends to integrate the concentrations of several of the other constituents. Of the six duplicate 2006 pairings with %RSD > 10, one pairing, from Bergona Lake in HO, had an extremely high %RSD, 406. As with the nitrate example given above, when constituent concentrations are low, small differences in concentrations can produce relatively large %RSD values. This is particularly accentuated for ANC, because laboratory determination of ANCs in the $\mu\text{Eq L}^{-1}$ range below 10 is somewhat problematic and typically more variable than for ANCs > $10 \mu\text{Eq L}^{-1}$. Bergona Lake had the lowest ANC recorded in 2006, with duplicate ANCs = 2.9 and $-5.9 \mu\text{Eq L}^{-1}$. The high %RSD is probably due to the extremely low ANC concentrations; no duplicate pairing for any other constituent at Bergona crossed the >10% threshold suggesting that the laboratory analysis of the Bergona sample was not problematic.

Almost one-third on the duplicate pairings with %RSD > 10 in 2006 are from two sets of duplicates, both from Powell Lake--one epilimnion and one outlet pairing. No other lake had more than 10% of its pairings with %RSD > 10. Both of the Powell Lake samples were collected on the same day. A third set of Powell Lake duplicates did not have many duplicates with %RSD > 10 nor did Powell Lake duplicates in prior years have high %RSD values. Presumably the same sampling crew collected the third Powell Lake set of duplicates. On this basis there does not appear to be any particular reason to be concerned that any particular lake, or sampling crew, was systematically associated with sample collection problems.

Although several lakes had %RSDs greater than 10 for several constituents, some of the %RSDs were only slightly above 10% (e.g., 11% to 13% for seven comparisons) and all lakes had %RSD > 10 for at least one constituent. The results of the %RSD analysis does not identify any particular lake as potentially having samples of questionable quality.

The mean absolute differences between the duplicates (the precision) for major chemical constituents are compared below for years 2003 through 2006:

Constituent	Unit	Mean Absolute Difference			
		2006	2005	2004	2003
ANC	$\mu\text{Eq L}^{-1}$	4.33	3.62	2.35	3.18
Conductivity	$\mu\text{S cm}^{-1}$	0.30	1.36	0.49	0.22
Calcium	$\mu\text{Eq L}^{-1}$	0.85	1.08	1.34	1.91
Magnesium	$\mu\text{Eq L}^{-1}$	0.30	0.29	0.80	0.72
Sodium	$\mu\text{Eq L}^{-1}$	0.29	1.12	2.70	0.72
Potassium	$\mu\text{Eq L}^{-1}$	0.26	8.81	1.91	0.34
Chloride	$\mu\text{Eq L}^{-1}$	0.17	7.94	0.16	0.62
Sulfate	$\mu\text{Eq L}^{-1}$	0.89	0.20	0.33	0.24
Nitrate	$\mu\text{Eq L}^{-1}$	0.20	0.03	0.25	0.09

In a study of lake waters on the Mt. Baker-Snoqualmie National Forest in Washington, Eilers et al. (1998) characterized samples with mean absolute differences $\leq 1.0 \mu\text{Eq L}^{-1}$ as dilute waters. Except for ANC, the 2006 Sierran samples match this criterion for dilute lake water.

Compared to the three earlier years, the 2006 results are generally lower for calcium, magnesium, potassium, chloride, and particularly sodium, and higher for nitrate, ANC and particularly sulfate. The three lakes with high ANC duplicate differences in 2006 either had particularly low or relatively high ANC (means of -2, 189 and $159 \mu\text{Eq L}^{-1}$). Its not surprising that lakes with these ANC ranges could have relatively large differences in ANC in duplicate samples. Similarly, two lakes with high sulfate (118 and $256 \mu\text{Eq L}^{-1}$) had sulfate differences between their duplicate samples over five times greater than the duplicate differences from any of the other 16 lakes with duplicated samples. Last, lakes synoptically sampled in 2006 in HO and JM Wildernesses generally had higher sulfate values than lakes sampled previously (see section 5.5 and Figure 9d). Simply because of these higher sulfate concentrations the potential for greater mean absolute duplicate differences in sulfate will be greater than for the previous years.

5.1.3 Bias -- Field Blanks

To help assure that water collection bottles are not contaminating samples, “field blanks” have water—typically de-ionized with very low or undetectable constituent concentrations—that is stored in the bottles for time periods comparable to the amount of time sample water remains in a bottle prior to analysis. Field blanks are typically sent out by the laboratory with the other bottles and taken to the field along with the actual sample

bottles. Common contaminants in the field blanks are sodium and chloride, from perspiration, or elevated acidity as a residue from prior cleaning of the bottle. The QA/QC protocol for the chemistry laboratory at the Riverside unit of the Forest Service's Pacific Southwest Research Station states that "[T]he value of a blank reading should be less than $\pm 0.05 \text{ mg L}^{-1}$ from zero" and Eilers et al. (1998) used $1.0 \text{ } \mu\text{Eq L}^{-1}$ for individual ions as a trigger value for blank contamination.

Nine field blanks were incorporated into the 2006 sample collection. Thirty-four of 81 constituent analyses (9 constituents for each blank) had detectable results, compared with 27 of 81 in 2005. As in other years a high proportion--eight of the nine--calcium samples had detectable concentrations, as did over one-half of the magnesium samples. Two of the 34 detections were $\geq 0.05 \text{ mg L}^{-1}$, PSW Riverside's threshold value. Both of these were for calcium, with concentrations equaling 0.091 and 0.053 mg L^{-1} . None of these detections had concentrations above 0.066 mg L^{-1} , only slightly above the threshold value. Eleven of the 34 detection were $\geq 1.0 \text{ } \mu\text{Eq L}^{-1}$, Eilers et al.'s (1998) criterion for individual ions. The highest concentration was $4.5 \text{ } \mu\text{Eq L}^{-1}$, and the four highest concentrations were for calcium. None of the detected concentrations were particularly high and the detections appear to be randomly distributed among the nine field blanks (in other words, no single sample/lake or samples had a preponderance of detections). The chemistry of two field blanks from HO with long transit times was not atypical of the chemistry of the non-HO blanks. Although there may be an issue with determination of calcium concentrations, there does not appear to be overwhelming evidence for a calcium problem. Potentially a problem with determination of calcium concentrations could relate to the ion imbalance that has persisted through all years of the monitoring program, or the water used in the field blanks may have relatively high calcium concentrations.

In summary, the field blank assessment does not appear to identify a systematic problem with sample collection. Nor does it identify any individual problematic samples or individual constituents.

5.1.4 Salt-contaminated Samples in 2005

In 2005 four samples, all from long-term monitoring lakes (Bullfrog-hypolimnion, Long-hypolimnion, Powell-hypolimnion and Lower Cole Creek-epilimnion), were initially labeled by RM staff as having "NaCl contamination". One of the four "contaminated" samples was a duplicate. The sample paired to the duplicate was not contaminated. Upon review of the data, RM staff decided that only one sample, from Lower Cole Ck Lake, was salt-contaminated. Although it had been a long-term monitoring lake, Lower Cole Ck Lake was not sampled in 2006. In 2006 the epilimnion (shallow) sample from Bullfrog Lake had moderately high chloride concentration (about four times greater than the sample with the second highest concentration). Sodium in the Bullfrog epilimnion sample was not high, however, and there's no other indication of salt contamination in the Bullfrog sample or any other sample from 2006.

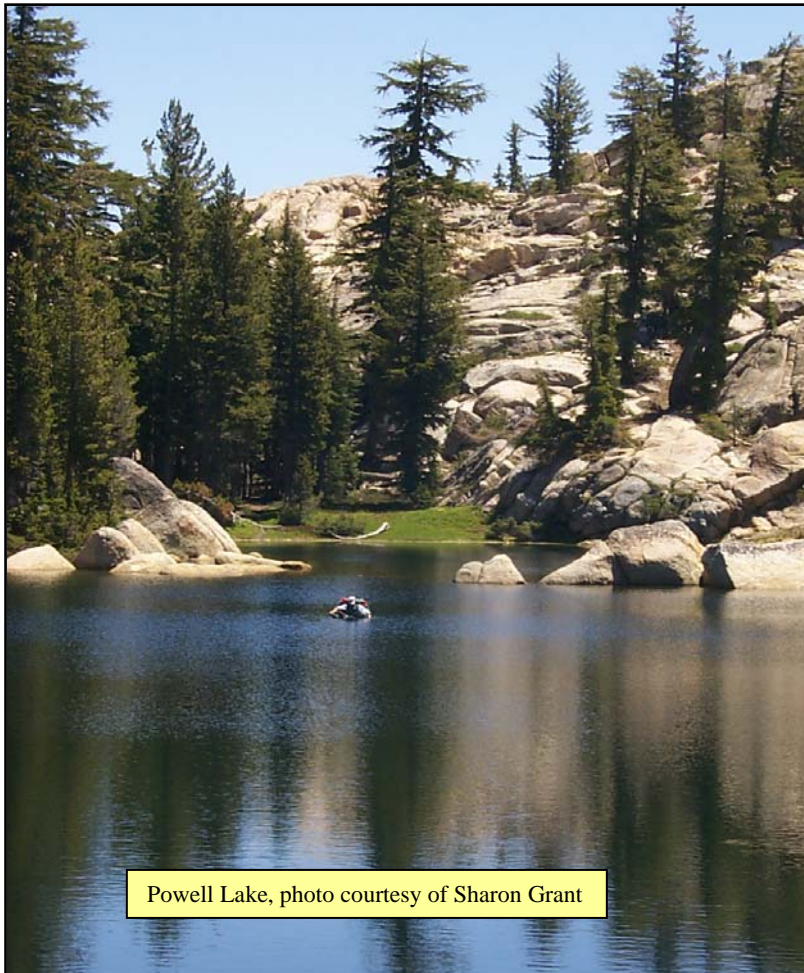
5.1.5 Summary of Quality Control Findings

The 2006 quality control analyses did not identify any new or unexpected issues. There were no outliers or salt-contaminated samples as in some earlier years. The ion imbalance identified in earlier years persisted in 2006. Although the chemistry of several samples collected in HO is atypical, the chemistries are not extreme. The long transit time for several HO samples may contribute to some of the atypical concentrations.

Analysis of a subset of the samples by a second laboratory in earlier years suggested that the cause for the ion imbalance is not necessarily a laboratory problem but is probably lack of analysis of one or more constituents that cause the current imbalance. Dissolved organic carbon is a candidate constituent that should be tested to help resolve the cause of the imbalance.

5.2 Time Trends for Long-term Monitoring Lakes

Five lakes have been monitored at least six times (see table on page 6), with one of these, Waca in Desolation Wilderness, sampled eleven times since 1985. A monitoring duration of 5 or 6 years is minimal for preliminary assessment of temporal change, and the literature suggests that typically a much longer time period is needed before temporal trends can be statistically verified. To offer a preliminary assessment of temporal change, plots of the chemistry of the five lakes are presented in Figure 8, and the results of a trend analysis are presented.



Powell Lake, photo courtesy of Sharon Grant

The magnitudes of concentration changes between years are typically small, on the order of one to a few $\mu\text{Eq L}^{-1}$. During development of the monitoring component of the Sierra Nevada Framework extensive research identified that annual ANC, sulfate and nitrate changes less than 30% would not be cause for alarm (personal communications, Al Leydecker and Jim Sickman 2000). The percent changes in Figure 8 are typically less than 30%, even for the very low concentrations levels

at which very low absolute differences would generate relatively large percentage differences.

The following table summarizes the results of the temporal trend analyses. Hyphenated cells signify a non-significant trend (at $\alpha = 0.10$). Numerical values are the Sen slope estimate (Sen 1968) of significant temporal trends based on the Mann-Kendall test (Gilbert 1987). A negative value signifies a significant downward trend so that, for instance, over the sampling period sulfate at Waca Lake decreased approximately $0.13 \mu\text{Eq L}^{-1}$ per year.

Lake	Constituent									
	ANC	Ca	NO ₃	SO ₄	Cl	K	Mg	Na	NH ₄	pH
Waca	--	-0.125	--	-0.13	--	--	--	--	0.057	--
Long	--	--	--	--	--	--	--	--	--	--
Powell	--	--	--	--	--	--	--	--	--	--
Key	--	--	--	--	--	--	--	--	--	--
Smith	--	--	--	-0.156	--	--	--	--	--	--

5.2.1 Waca

Waca Lake is located immediately west of the crest of the Sierra Nevada at approximately 2495 m elevation about 12 km southwest of Lake Tahoe. It is one of many adjacent lakes in the Desolation Valley section of Desolation Wilderness. Waca is a headwater lake in granodiorite terrain with very little vegetation on its watershed. The lake occupies about 2 hectares within a 10-hectare, south-west facing watershed.

Waca Lake has the longest monitoring record, now eleven samplings, starting with the Western Lake Survey in 1985 (Figures 8a and 8b). The downward trend in sulfate, first identified at Waca in 2004, parallels the general trend downward in the atmospheric wet deposition and sulfate concentration recorded at long-term deposition monitoring locations in Yosemite and Sequoia-Kings Canyon National Parks (NADP 2006). At Waca sulfate concentrations in the $4\text{-}6+ \mu\text{Eq L}^{-1}$ range between 1985 and 1993 have more recently dropped to the $2\text{-}3+$ range, with the lowest recorded value, $1.7 \mu\text{Eq L}^{-1}$ in 2006.

Calcium has decreased at a statistically significant rate, and ammonium has increased at a statistically significant rate at Waca Lake over time. The changes are small and for calcium may be influenced by one very low value ($0.6 \mu\text{Eq L}^{-1}$) in 2004. In 2005 and 2006 ammonium was above $1 \mu\text{Eq L}^{-1}$ for only the second and third times in the eleven-sample set.

Neither Waca Lake, nor any of the other Sierran lakes assessed here, show a significant temporal trend (at $\alpha = 0.10$) for nitrate or ANC, two important indicators of potential acidification or undesirable nitrogen fertilization. Theoretically, increases in sulfate and nitrate, and a decrease in ANC over time, could be a precursor to acidification, although alternative explanations for changing levels of these constituents are possible.

The 30% change criterion, mentioned above as an indicator of potential concern, is met for sulfate and marginally for ANC. These higher percent changes are not believed to foretell acidification because (1) sulfate is decreasing over time, rather than increasing as would be expected as a precursor for acidification, and (2) a single low ANC concentration, from 2001, causes the 30% criterion to be triggered. The low concentration is followed in 2002 through 2006 with ANC levels similar to prior years. ANC concentrations in the 1-2 $\mu\text{Eq L}^{-1}$ range (as in 2001) are at the edge of the resolution band for typical laboratory analysis; values in this range are less reproducible than higher values.

5.2.2 Key

Key Lake, located in the north-central portion of Emigrant Wilderness at 2799 m elevation and almost due east of San Francisco, drains a west-facing catchment approximately 6 hectares in area. This headwater lake is also small, at 1 hectare area. The bedrock geology is similar to much of the Sierra Nevada dominated by felsic materials such as granodiorite, diorite, tonalite and felsic gneiss and schist. There is very little vegetation in the Key Lake watershed.

ANC dropped at Key Lake from the 8-10 $\mu\text{Eq L}^{-1}$ range between 2000 and 2003 to less than 1.4 $\mu\text{Eq L}^{-1}$ in 2004 and 2005, causing a significant change in ANC at Key Lake for the six survey years from 2000 to 2005, but the 2006 value “rebounded” to the historical maximum (Figure 8c). There were no statistically significant changes in 2006 for ANC, sulfate or nitrate at Key Lake. Data from future years are needed before interpreting further the ANC changes.

Some of the year-to-year ANC, sulfate and nitrate differences meet the 30% triggering value. However, except for ANC, the absolute value of the yearly differences are small, typically less than 2 $\mu\text{Eq L}^{-1}$, and probably not realistically significant.

None of the constituent concentrations plotted in Figure 8d show an obvious trend through time; increases are typically followed by decreases (or vice versa), and none of the trends are statistically significant.

5.2.3 Long

Long Lake occupies a moderately large (63 ha), north-facing headwater catchment in the northeastern section of Kaiser Wilderness about 75 km northeast of Fresno. At 2725 m elevation Long Lake is in the same general elevation range as the other four lakes assessed for temporal trends. It has more vegetation than many other Sierran wilderness lakes, with about one-half of the granodiorite-dominated catchment in vegetation identifiable from aerial photos. The lake occupies about 3.8 ha area and is backed by a 400-m headwall immediately due south.

ANC at Long Lake is higher than at the other four lakes addressed in this section, and ranged from the high 20 to high 30 $\mu\text{Eq L}^{-1}$ between 2000 and 2006 (Figure 8e). Calcium and sodium concentrations are also slightly higher at Long than the other three lakes. No trends through time are identified for this lake, and any incipient increases through time—for instance for sodium and potassium between 2000 and 2004—were negated by downturns in 2005 (Figure 8f). Except for ANC, year-to-year changes for the other constituents have typically been 1 to 2 $\mu\text{Eq L}^{-1}$ and none of the annual ANC, sulfate or nitrate concentration changes meet the 30% criterion.

5.2.4 Powell

Powell Lake drains a north-facing, 32-ha catchment in the western portion of Emigrant Wilderness. This headwater lake is slightly lower down on the western slope of the Sierra than most other long-term monitoring lakes in the LAKES network. Powell's area is about 1.6 ha and its elevation is 2685 m. As with the other lakes detailed here, Powell's catchment is dominated by granodiorite. Almost one-half of the catchment is well-vegetated.

No statistically significant trends through time were identified for any chemical constituent. Similar to Long Lake, at Powell there has been very little variation through time in conductivity, magnesium, potassium, ammonium and sulfate (Figures 8g and h). Similar to many Sierran lakes nitrate concentrations have been very low, and at Powell were below the detection limit for all five surveys between 2000 and 2005. None of the annual ANC, sulfate or nitrate concentration changes at Powell Lake meet the 30% criterion.

5.2.5 Smith

Smith Lake, located about 4 km west of Waca Lake at the western edge of Desolation Wilderness, lies in a west-facing catchment with a 300-m headwall immediately east of the lake. The 2649 m elevation lake occupies about 10% of its 35-ha granite-dominated catchment. Mapping software identifies Smith Lake as dammed. Field work is needed to determine if there really is a dam here and if so its composition. A wooden dam is probably acceptable, but potentially chemicals from a cement dam could confound assessment of atmospheric effects on the lake's chemistry.

Besides Waca Lake, Smith Lake is the only long-term lake with a significant temporal trend for any constituent, in this case sulfate. As with Waca, the trend is relatively small, 0.156 $\mu\text{Eq L}^{-1} \text{ yr}^{-1}$. Sulfate concentrations dropped from the 6-8 $\mu\text{Eq L}^{-1}$ range in the mid-1980s to the 4-5 $\mu\text{Eq L}^{-1}$ range recently. To varying degrees, ANC, calcium, sodium and magnesium share decreasing and increasing ionic concentration patterns through time (Figures 8i and j). The patterns may be due partly to potentially differing sampling protocols and (or) laboratories analyzing the samples. For instance at Smith Lake in 1985 and 1986 the samples were analyzed by K. McCleneghan, a contract researcher for the California Air Resources Board (McCleneghan et al. 1987), in the early 1990s by the University of California, Santa Barbara, and since then by RM.

5.3 Lake Chemistry Differences Among Class I Areas

5.3.1 Introduction

Almost 170 lakes in eleven Wildernesses have been sampled since the LAKES project began in 2000. These Wildernesses span 600 airline kilometers from Modoc County in northeast to the southeastern tip of the Sierra Nevada and occupy both a wide range of biogeochemical environments and atmospheric deposition regimes. Although the Wildernesses were all synoptically sampled to provide a basis for selection of long-term monitoring lakes, specific lakes were chosen for sampling for differing reasons among the Wildernesses. As such the chemistry results are not strictly comparable among Wildernesses. For instance, Wildernesses with a relatively small number of lakes (South Warner (SW), Kaiser (KA) and 1000 Lakes (TL)) were censused—all lakes in these Areas were sampled. In Wildernesses with more lakes (JM, HO, Ansel Adams (AA), Mokelumne (MO) and Caribou (CA)), lakes were selected for low ANC or to be more representative of lakes in the Wilderness (e.g., Emigrant (EM) where lakes on both granitic and volcanic terrain were purposively sampled). One ramification of these different lake selection criteria is that JM, HO, AA, MO and CA Wildernesses would be expected to have lower ANCs than the others because the lakes sampled in these Wildernesses were modeled to have low ANC. Also the chemical variability would be expected to be greater in the censused Wildernesses and Emigrant where a broader spectrum of lake chemistries were presumably sampled. Last, sample size differences could influence the results; thirteen times as many lakes were sampled in EM as in Dinkey (DN) (Figure 9a).

In the future lake monitoring will focus exclusively on approximately twenty long-term monitoring lakes; no other lakes will be sampled synoptically. Because the synoptic effort is now finished this report concludes the analysis of the synoptic lake dataset and provides a more comprehensive assessment of the synoptic dataset than previous annual reports. Information on differences among the chemistries of the lakes in the various Areas can contribute to an improved understanding of lake dynamics as a better basis for management decisions. For instance, synoptically-based chemistry groupings of Areas could simplify the interpretation of impacts from atmospheric deposition or other anthropogenic disturbances/perturbations.

5.3.2 Theoretical Lake Chemistry Similarities Among Class I Areas

Although the main focus of this report is the interaction of atmospheric deposition and Wilderness lake chemistry, other factors confound this relationship. For instance, although downwind proximity to known atmospheric emission sources will influence lake chemistry, catchment geology and other watershed factors are major contributing determinants to lake chemistry. Deposition and catchment factors influencing lake chemistry include:

- Atmospheric
 - Proximity to known emission sources

- Proximity to other anticipated sources for different deposition characteristics
- Catchment/geologic
 - Major geomorphic provinces: Southern Cascades, Central Sierra Nevada, Southern Sierra Nevada, Great Basin

Each Wilderness can be characterized by one or more of these factors. For instance, SW is on the western edge of the Great Basin physiographic province—and may therefore receive calcareous deposition from basins to the east. It is distant from anthropogenic emission sources and its geological composition is primarily volcanics overlaying sedimentary layers. In contrast, DE, on the western slope of the Sierra Nevada, is downwind of the Sacramento metropolitan area, and is dominated by large expanses of bare granitic rock. The eleven Wildernesses are characterized by deposition and geologic factors as follows:

Area	Upwind Anthropogenic Emissions	Great Basin Atmospheric Deposition Influence	Geomorphic Province/ Location
S Warner	Low	Mod/high	Great Basin
1000 Lakes	Low	None/low	Southern Cascades
Caribou	Low	None/low	Southern Cascades
Desolation	High	None/low	West-central Sierra
Mokelumne	Mod	None/low	West-central Sierra
Emigrant	Mod	None/low	West-central Sierra
Hoover	Low	High	East-central Sierra
Kaiser	High	None/low	West-central Sierra
Ansel Adams	Mod	Mod	Southern Sierra, east & west
Dinkey	High	None/low	West-central Sierra
John Muir	Mod	Mod	Southern Sierra, east & west

This categorization is simplistic; complex and interacting factors, and secondary influences, are important. For instance, lakes in AA and JM lie on both sides of the Sierran crest and potentially are affected by differing emission sources on the west slope (e.g., the Fresno eddy bringing anthropogenic pollutants from the San Joaquin Valley) and the east slope (natural calcareous inputs from the Owens Valley or other dry basins). Geologies can differ from the east to the west slope, with some areas of the Sierra Nevada retaining sedimentary “roof pendants” at and near the crest with chemical characteristics different from the main granitic mass of the Sierra Nevada batholith. Large Wildernesses spanning both sides of the crest could therefore be expected to have more variable lake chemistries than small Wildernesses located solely on the east or west slope. Given these caveats the following grouping of Areas is proposed:

- S Warner/ Hoover
- 1000 Lakes/Caribou
- Desolation/Mokelumne/Emigrant
- Kaiser/Dinkey

- Ansel Adams/John Muir

These groupings are preliminary. In particular the eastern portions of AA and JM could be grouped with SW and HO as an “eastern” grouping. DE’s location in a relatively high deposition pathway compared to MO and EM could warrant segregation of these three Areas into two groupings. On balance this preliminary categorization is meant to identify a smaller rather than larger number of groups.

5.3.3 Data Analysis Procedures

Because the chemical constituents in several of the individual Wilderness datasets are not normally distributed nonparametric statistics are used to compare the lake chemistries. Median and interquartile range information, as well as the mean, are displayed for ANC, calcium, nitrate and sulfate in Figure 9a-d. ANC is displayed as the single best gauge of sensitivity to acidification. Calcium is representative of alkaline inputs. The atmosphere is the primary source of nitrate in wildlands and sulfate represents acidic inputs that can have an atmospheric or geologic source. In the Figure 9 “box and whisker” plots the horizontal line designates the median, the plus sign designates the mean, and the interquartile range (25th and 75th percentiles) is designated by the upper and lower ends of each box. “Whiskers” extend to the maximum and minimum values.

5.3.4 Results

At the 0.05 level of statistical significance, the SW/HO group had higher concentrations of ANC, calcium, nitrate and sulfate than the remaining Wildernesses combined as a second group. The following table summarizes other “pairwise” comparisons between the designated group and all other Wildernesses combined. In the table “>” means statistically greater at the 0.05 level, “<” means statistically less, “N” means not statistically different and “=” means statistically different but with medians of very similar magnitude (e.g., very low nitrate concentrations).

Group	ANC	Ca	NO ³	SO ⁴
SW/HO	>	>	>	>
TL/CA	>	N	=	<
DE/MO/EM	<	<	=	<
KA/DN	N	N	=	N
AA/JM	N	>	>	>

This analysis suggests that several of the groupings proposed in section 5.3.2 may be real, in particular the SW/HO grouping wherein all four statistical tests were significant. The KA/DN group could probably be collapsed into either the DE/MO/EM or possibly the AA/JM group because most statistical comparisons with the KA/DN group were not significantly different.

Because of the geographical isolation of SW from the other Wildernesses, SW was compared to a grouping of the other 10 Areas. At the 0.05 level statistically significant differences in concentrations were identified for ANC, calcium, conductivity, potassium,

magnesium, sodium and ph, but not chloride, ammonium, nitrate and sulfate, suggesting that SW may be receiving more alkaline inputs than the other Wildernesses.

Rather than relying on nonparametric analysis among Wildernesses as the sole differentiating approach, ANC and nitrate distributions by Wilderness are compared in Figures 10 and 11. These graphs relate the percentage of samples in each Wilderness with concentrations less than any specified concentration. For instance, 70% of the JM samples had nitrate concentrations less than about $6 \mu\text{Eq L}^{-1}$. For the same 70% “benchmark” all other Wildernesses had much lower nitrate concentrations, and for several Wildernesses over 70% of their samples had undetectable (0) nitrates.

From Figure 10, SW is clearly distinctive from all other Wildernesses in having much higher ANC values. Furthermore, at least one-half of the lakes sampled in all other Wildernesses had ANCs less than $50 \mu\text{Eq L}^{-1}$, a value identified by Sullivan (2001) as the ANC level above which Sierra Nevada lakes probably protected from foreseeable episodic acidification. Wildernesses with lakes having ANCs below $50 \mu\text{Eq L}^{-1}$ are therefore at greater risk than SW in terms of potential acidification. Among the non-SW Wildernesses, DN, DE and AA have either all or a preponderance of their samples lakes with $\text{ANC} < 50 \mu\text{Eq L}^{-1}$, suggesting these Wildernesses may be particularly sensitive to acidification. EM and JM have several high-ANC lakes probably because lakes in volcanic terrain were sampled in EM, and lakes influenced by atmospheric influxes of dust from east of the Sierra were sampled in JM.

JM and AA have a higher percentage of their lakes with relatively high nitrate concentrations than most other Areas (Figures 9c, 9d and 11). Reasons for this segregation aren't clear but potentially the higher nitrate/sulfate lakes may be located east of the Sierran crest in an atmospheric deposition regime, or geologic condition, that differs from that to the west.

5.3.4.1 Elevated Concentrations East of the Sierran Crest

In 2005 lakes east of the Sierran crest in JM and AA had higher nitrate and sulfate than lakes in Wildernesses west of the crest (except SW, which also is located east of crest of the southern Cascades). In 2005 several hypothetical causes were advanced for the elevated nitrate and sulfate concentrations in the east. These include:

- Nitrate and sulfate concentrations have changed recently across the Sierra Nevada and this change is seen primarily in the three most recently sampled Wildernesses, HO, AA and JM.
- The modeling was less effective in AA, HO, JM and SW in identifying dilute lakes so that the lakes sampled in these Wildernesses have higher concentrations than in the lakes sampled earlier in the monitoring program.
- Lakes have higher nitrate and sulfate concentrations in the east than in the west, potentially due to atmospheric deposition from alkaline sources in the Great Basin and/or geological sources of chemical constituents that would otherwise be of low concentration (e.g., sulfate).

- A small number of unrepresentative lakes in AA and JM force higher mean and standard deviations for nitrate and sulfate.

With completion of the synoptic sampling this year's analysis follows up the 2005 assessment to more comprehensively investigate potential chemical differences between east and west of the crest.

“Eastern lakes” are defined as all of those in SW and HO and those east of the Sierran crest in JM and AA, with all other lakes “western lakes”. With these groupings, statistically significant differences (using the Wilcoxon Rank Sum procedure—two-tailed) exist for all constituents at the 0.2, 0.1 and 0.05 level except magnesium, which has non-significant differences at all of those levels. In particular, ANC, calcium, nitrate and sulfate all have statistically higher concentrations east versus west of the mountain crest. Figure 12 plots the cumulative distributions for ANC, calcium, nitrate and sulfate for the western and eastern groups. There are clear differences—concentrations for all four constituents are much lower in the western group than the eastern group.

With the information currently available, it's not possible to conclusively determine the cause for the higher nitrate and sulfate east of the mountain crest. However, the second explanation is not supported by the ANC data in that the mean and median ANC for AA and JM is similar to the mean ANC of most other Wildernesses (Figure 9a). Lakes on the eastern side of both AA and JM have higher sulfate and nitrate concentrations than lakes west of the Sierran crest. SW, with relatively high mean nitrate and sulfate concentrations, is also located in eastern California. Potentially atmospheric pathways with sources in the alkaline Great Basin are influencing these eastern lakes, and are therefore the cause of the higher means and standard deviations for nitrate and sulfate in these three Wildernesses.

The variability in concentrations at JM and HO, and to a lesser extent in SW and AA lakes, is generally greater than in the “west-side only” Wildernesses. This may also be influenced by the east-west nature of the distribution of lakes in JM and AA. Higher nitrate and sulfate exist east of the Sierran crest in the JM and AA lakes. Combining relatively high concentrations for east-side lakes with relatively low concentrations for west-side lakes produces high variability overall.

5.3.4.2 Elevated Sulfate in Lakes West of Mono Lake

In 2004 two lakes, Dana and Kidney, located at the northern end of AA, had high sulfate and nitrate concentrations. Several lakes sampled this year in HO had even higher sulfate concentrations, in the 100 to 250 $\mu\text{Eq L}^{-1}$ (Figure 9d). These lakes are immediately east of lakes sampled in 2003 by David Clow (personnel communication) having sulfate concentrations in the 80-100 $\mu\text{Eq L}^{-1}$ range. These ranges of sulfate concentrations are an order of magnitude or more greater than typical for lakes sampled in the LAKES project. The cause(s) of the high sulfate is unknown but thought to be geologic. Some of the high-sulfate lakes in HO are within one mile of low-sulfate lakes, suggesting that atmospheric pathways would need to be very localized to bring appreciable sulfur-

bearing compounds to one lake but not another lake a mile distant. With one exception, the high-sulfate lakes in HO have high or relatively high ANC. The exception, Bergona Lake at the northern edge of the suite of lakes sampled in HO, had extremely low ANC (mean of two duplicates = $-1 \mu\text{Eq L}^{-1}$), coupled with a sulfate concentration of $101 \mu\text{Eq L}^{-1}$.

6.0 Candidate Long-term Monitoring Lakes for John Muir and Hoover Wildernesses

Prior discussions call for establishment of seven long-term monitoring lakes in JM, based upon the number of lakes in JM and the large size of JM (e.g., 234,854 hectares vs. 93,184 hectares for the second-largest Area, AA). Because HO is not formally a part of the California region of the Forest Service, and because prior discussions have focused primarily on the California Region, a target number of long-term monitoring lakes for HO needs to be discussed. Forty-two lakes were modeled for ANC in HO prior to field sampling. This number (42) is slightly greater than the number of lakes in CA, 35, and less than the number in EM (95). The long-term monitoring network incorporates one Caribou lake and three Emigrant lakes. On this basis HO would be allocated between one and two long-term monitoring lakes.

6.1 Hoover

Ten lakes were sampled synoptically in 2006 as the candidate pool for selection of long-term monitoring lakes in HO. Four of these had $\text{ANC} \leq 20 \mu\text{Eq L}^{-1}$ (Bergona=3, Cascade=10, Z=19 and South Mill=20) and another four had $\text{ANC} > 85 \mu\text{Eq L}^{-1}$ (Figure 2). Cascade, Z and S Mill are near each other northeast or north of Saddlebag Lake at the southern edge of the Wilderness. They all appear to have fairly easy access with defined trails at least partway to each lake from the north shore of Saddlebag Lake (outside the Wilderness). These three lakes are all less than about 2.5 km from a trailhead with Z being about 1.2 km distant from Saddlebag Lake, which potentially has boat access to its northern shore. On a 1:24,000 scale topographic map Cascade appears to have the most classically-defined catchment; S Mill is immediately below N Mill and the topography around Z appears hummocky. Bergona appears to be about 4 km from the nearest trailhead with about a 760 m elevation gain from the trailhead. On the basis of low ANC, ease of access, catchment shape and headwater location Cascade Lake appears to be a good candidate for long-term monitoring.

6.2 John Muir

Because of the long north-south extent of JM, the positioning of JM on both sides of the Sierran crest, and therefore the likelihood of a variety of atmospheric pathways relevant to JM, a reasonable objective is to spread the long-term monitoring lakes both north-south and east-west across the Wilderness. The following discussion presumes this objective and does not address other issues. For instance, lakes meeting the north-south/east-west objective may not be readily accessible.

Four of the five lakes with the lowest ANC are grouped at the west-central section of JM, immediately east of Courtright and Wishon Reservoirs. From a purely “low-ANC” perspective one of these lakes (e.g., Bullet at $15 \mu\text{Eq L}^{-1}$ ANC), plus Stanford, Treasure or Dade on the northeast, Marshall on the northwest, Thunder and Lightning on the east-central, and Bench on the southeast give a broad spatial coverage and keep ANC below $36 \mu\text{Eq L}^{-1}$ (except for Bench at $51 \mu\text{Eq L}^{-1}$). The chemical concentrations for the synoptic samples from these lakes are within the expected range, except for moderately high nitrate at Stanford Lake and moderately high sulfate at Thunder and Lightning Lake. None of the lakes sampled in 2006 in the extreme southern portion of JM has ANC below $89 \mu\text{Eq L}^{-1}$ (Cottonwood 5B, Figure 1). Cottonwood 5B’s non-ANC chemistry is typical of other moderate-ANC lakes in the Sierra Nevada and its extreme southern location is approximately 50 km due east from wet and dry deposition monitoring sites in Sequoia National Park. Cottonwood 5B could be a reasonable lake for long-term monitoring, particularly if an aim is to be relatively close to deposition monitoring sites and to monitor a location as far south as possible within the FS Class I Area jurisdiction.

7.0 Options for Refining the Sample Collection Procedures – Outlet Sampling in Early Autumn

Most lake sampling in mountainous areas of the United States (e.g., Western Lake Survey) is undertaken in late summer or early autumn, probably for two reasons: (1) logistical accessibility and (2) thermally mixed lake waters. Thermal mixing means that the lakes have “turned over” and there is mixing at all depths. Earlier sampling can encounter thermally stratified lake waters, with differing chemistries in shallow versus deeper zones of the lake. To characterize completely the chemistry of a thermally mixed lake, samples should be taken from the main thermal zones, typically including a sample near the bottom of the lake. This requires sampling from somewhere on the lake itself. In thermally mixed lakes a single sample, at the lake outlet or shoreline, is generally assumed to adequately represent the lake chemistry.

The primary current aim of Project LAKES is to identify changes in acid-base chemistry. Extensive earlier research (Melack et al. 1998) at several Sierran lakes identified early summer as the time when the single best indicator of acidification, ANC, is at its annual low. Quantification of ANC at any time other than either the annual low or annual high point could add substantial within-year variability; the ANC value would be some unknown “distance” between the annual maximum and minimum. The annual low best characterizes lake sensitivity to acidification. Consequently the LAKES project targeted early summer sampling. The early summer period trades off the potential for thermal stratification—with the consequent need for both shallow and deep lake sampling in order to completely characterize lake chemistry—with the benefit of a tighter quantification of ANC.

An alternative to early summer sample collection is collection after the turn-over, to simplify and reduce the cost of sample collection, at the risk of obfuscating the quantification of ANC. The ramifications of such a switch need to be comprehensively

understood and debated. To begin to assess potential differences in lake chemistry at LAKES project lakes over the summer and early autumn period, in 2006 samples were collected (1) at several long-term monitoring lakes two or three times and (2) at both mid-lake and outlet locations.

7.1 Chemical Differences Between Early Summer and Late Summer

Insufficient sampling was undertaken to completely characterize within-year differences. Consequently only preliminary, graphical information is presented; no statistical assessment is undertaken

Samples were collected three times in 2006 at Long Lake and Powell Lakes, in KA and EM respectively. At these locations sulfate and nitrate generally decreased through time while ANC and calcium generally increased (Figure 13). This general trend matches results of extensive analysis of seasonal changes by University of California, Santa Barbara researchers in the 1980s (Melack et al. 1998). More within-year sampling, ideally at the traditional end-of-snowmelt period and late September or early October when the lakes should be thermally mixed, is needed to better quantify within-year concentration differences.

7.2 Chemical Differences Between Outlet and Mid-lake Sampling Locations

In 2006 twelve pairs of epilimnion and outlet samples were collected at long-term monitoring lakes. Two similar pairs were collected in earlier years. For this fourteen-sample dataset significant differences were not identified (at the 0.05 level) for ANC, nitrate or calcium using the Wilcoxon paired sign test. Significant differences were identified, however, for sulfate. In five paired outlet and hypolimnion samples from 2006, ANC and calcium differed significantly but sulfate and nitrate did not. Small sample sizes, for hypolimnion-outlet comparison in particular, so results are preliminary and it is premature to speculate on causes for these results.

8.0 Topics from Previous Years

Three aspects of the monitoring program that have been previously discussed are (1) the option to sample at lake outlets or along the shoreline, (2) concerns with the ongoing ion imbalance and (3) analysis of the zooplankton samples. Progress on the option for outlet sampling is discussed above; there has been no change since the 2004 report on the other two issues and the recommendations from 2004 remain current:

- Consider analyzing a sub-set of the 2007 samples for dissolved organic carbon. DOC sampling requires separate bottles and cannot be done at the RM lab. Therefore more coordination would be needed prior to sample collection than otherwise. Cost for DOC analysis is approximately \$50 per sample, without transportation costs.
- Analyze the collected zooplankton data and discuss pros and cons of continued transparency and zooplankton collection in terms of potentially replacing mid-lake sample collection with outlet sample collection.

9.0 Conclusions

After collection of chemistry information from 170 synoptically-sampled lakes between 2000 and 2006, the network of long-term monitoring lakes should be completed in 2007. Completion of the network will reduce the expense of monitoring and extend the ability to identify temporal and spatial trends in lake chemistry changes at eleven Wildernesses in the Sierra Nevada and northeastern California.

The overall quality of the 2006 laboratory analysis improved with respect to 2004 and 2005. Application of commonly-used quality assurance techniques identified no issues other than continuation of a long-standing imbalance between cations and anions and the overly long transit time for samples from Hoover Wilderness. Recommendations are given to address the ionic imbalance at the beginning of this report.

Except for five lakes, the duration of the monitoring is insufficient to quantify any temporal trends in the acid-base chemistry of the lakes. Statistically significant changes in lake chemistry were identified for calcium, sulfate and ammonium at one lake and sulfate at a second lake. The sulfate concentration decreases may reflect documented reductions in sulfur deposition in many locations in the United States. The calcium and ammonium changes are minor. These results are preliminary and could change as more data are collected.

Lakes in Wildernesses located to the west of the crest of the Sierra Nevada generally have similar chemistries. South Warner and Hoover Wildernesses and parts of Ansel Adams and John Muir Wildernesses are more directly exposed to atmospheric deposition originating in the drier, more alkaline Great Basin terrain east of the Sierra crest. Nitrate and sulfate concentrations at these lakes are higher and more variable than at Wildernesses located exclusively on western slope of the Sierra Nevada.

There is a potential to revise the monitoring protocol to sample only from lake outlets in early autumn. This is premature at this time and additional paired outlet and mid-lake samples should be collected in during both the traditional early summer sampling period and in early autumn to help address this alternative. Also the zooplankton data collected to date should be analyzed before a decision is made to abandon mid-lake sampling.

Acknowledgements

This report benefited from discussions with Joseph Gurrieri and borrowed liberally for the approach to statistical analyses from his report on High Uinta lake quality (Gurrieri 2006).

References Cited

Berg, N.H. 2002. Sierra Province Adaptive Monitoring Program – Lake monitoring in Sierra Nevada Class I Wilderness areas. USDA Forest Service Pacific Southwest Region. Unpublished report on file at the Pacific Southwest Research Station, Albany, CA.

Berg, N.H. and S. Grant. 2002. Project LAKES – Lake sampling protocols for synoptic surveys. USDA Forest Service Pacific Southwest Region. Unpublished report on file at the Pacific Southwest Research Station, Albany, CA, and the Stanislaus National Forest, Sonora, CA.

Berg, N.H. and S. Grant. 2004. Project LAKES – Long-term water quality monitoring and zooplankton data collection protocol. USDA Forest Service Pacific Southwest Region. Unpublished report on file at the Pacific Southwest Research Station, Albany, CA, and the Stanislaus National Forest, Sonora, CA.

Berg, N.H., Gallegos, A., Dell, T., Frazier, J., Procter, T., Sickman, J., Grant, S., Blett, T. and M. Arbaugh. 2005. A screening procedure for identifying acid-sensitive lakes from catchment characteristics. *Environmental Monitoring and Assessment* 105:285-307.

Clow, D.W., Striegl, R.G., Nanus, L., Mast, M.A., Campbell, D.H. and D.P. Krabbenhoft. 2002. Chemistry of selected high-elevation lakes in seven national parks in the western United States. *Water, Air and Soil Poll.: Focus* 2:139-164.

Dixon, W.J. 1953. Processing data for outliers. *Biometrics* 9:74-89.

Eilers, J., Gubala, C.P., Sweets, P.R. and K.B. Vache. 1998. *Limnology of Summit Lake, Washington—its acid-base chemistry and paleolimnology*. Prepared for the Mt. Baker-Snoqualmie National Forest, Mountlake Terrace, WA. E&S Environmental Chemistry, Inc. Corvallis, OR. 61 p. plus appendices.

Eilers, J. 2003. *Water Quality Review of Selected Lakes in the Northern Rocky Mountains*. J.C. Headwaters, Inc. Bend, Oregon. February 2003. 19 p.

Fenn, M.E., Baron, J.S., Allen, E.B., and others. 2003. Ecological effects of nitrogen deposition in the western United States. *BioScience* 53:404-420.

Gilbert, R. 1987. *Statistical Methods for Environmental Pollution Monitoring*. Van Nos Reinhold.

Gurrieri, J. 2006. DRAFT Data Analysis Protocol for Long-term Lake Monitoring. Unpublished report on file at the Intermountain Regional Office, USDA Forest Service, Ogden, UT.

Kanciruk, P., Gentry, M., McCord, R., Hook, L., Eilers, J. and M.D. Best. 1986. *National Surface Water Survey: Eastern Lake Survey-phase I, Data Base Dictionary*. Oak Ridge National Laboratory, Environmental Sciences Division Publication 2778. ORNL/TM-101153.

Landers, D.H., Eilers, J.M., Brakke, D.F., Overton, W.S., Kellar, P.E., Silverstein, M.E., Schonbrod, R.D., Crowe, R.E., Linthurst, R.A., Omernik, J.M., Teague, S.A. and E.P. Meier. 1987. *Western Lake Survey Phase I. Characteristics of Lakes in the Western United States. Volume 1: Population descriptions and physico-chemical relationships*. US EPA, Off. Research and Development, Washington DC. EPA/600/3-86/054a (January 1987). 176 p.

McClenaghan, K., Imai, R.H., King, J.T. and S.J. Boggs. 1987. *Statewide Survey of Aquatic Ecosystem Chemistry: 1986*. California Department of Fish and Game, Environmental Services Branch, Fish and Wildlife Water Pollution Control Laboratory, Rancho Cordova, CA. Lab. Rept 86-5, September 1987.

Melack, J.M., Sickman, J.O. and A. Leydecker. 1998. *Final Report. Comparative Analyses of High-Altitude Lakes and Catchments in the Sierra Nevada: Susceptibility to acidification*. Prepared for the California Air Resources Board, Contract A032-188.

Musselman, R.C. and W.L. Slauson. 2004. Water chemistry of high elevation Colorado wilderness lakes. *Biogeochemistry* 71:387-414.

NADP (National Atmospheric Deposition Program). 2006. National Trend Network. Accessed 11/16/06 at <http://nadp.sws.uiuc.edu/sites/sitemap.asp?state=CA>.

NIC (National Information Consortium). 2005. *WQSTAT Plus User's Guide*. NIC Environmental Division, 10540 S. Ridgeview Rd., Olathe, KS.

Sen, P.K. 1968. Estimates of the regression coefficient based on Kendall's tau. *Journal of the American Statistical Association* 63:1379-1389.

Sickman, J.O., Melack, J.M. and D.W. Clow. 2003. Evidence for nutrient enrichment of high-elevation lakes in the Sierra Nevada, California. *Limnology and Oceanography* 48:1885-1892.

Sullivan, T.J., Peterson, D.L., Blanchard, C.L., Savig, K. and D. Morse. 2001, *Assessment of Air Quality and Air Pollutant Impacts in Class I National Parks of California*. USDI National Park Service, Air Resources Division, Denver CO. April 2001.

Turk, J.T. 2001. *Field Guide for Surface Water Sample and Data Collection*. Air Program, USDA Forest Service. June 2001. 67 p.

US EPA, Off. Research and Development, Washington DC. EPA/600/3-86/054a. January 1987. 176 p.

US EPA. 1989. *Statistical Analysis of Ground-water Monitoring Data at RCRA Facilities. Interim Final Guidance*. Off. Solid Waste, Waste Manage. Div. Washington, DC.

US Senate. 1977. *Senate Report 95-127*. 95th Congress, 1st session.